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On the lattice vibrations and specific heat of KCl and NaCl at low temperatures

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With 6 figures in the text

SUMMARY

The frequency spectrum at 0°K and the specific heat at low temperatures have been calculated in three different approximations. The Born model is shown to give results which are definitely not in accordance with experiments. A second approach which has some theoretical support in the Heitler-London treatment of ionic crystals gives considerably better results. Finally, this approach has been supplemented by taking the polarisability of the ions into account. The polarisation is shown to have a strong influence upon the frequency distribution. The results in this approximation are those which best agree with the observed specific heats, although some discrepancy still remains.

Introduction

The frequency distribution of thermal vibrations and the specific heat at low temperatures for KCl and NaCl have earlier been investigated by Kellermann [7] and Iona [6]. Both investigations were based on the Born model, i.e. a long range Coulomb attraction between the ions and a short range repulsive central force. The agreement between the calculated and observed specific heat was remarkably good in both cases. This fact has often been considered as a confirmation of the approximate validity of the assumptions inherent in the Born model. The significance of their results must, however, be questioned for the following reason. The force constants associated with the repulsive forces were in both investigations chosen so as to fit the elastic constants at room temperature. The calculated frequency distribution must therefore be considered as an approximation to that at room temperature. The comparison with experiments, however, concerns the specific heat at low temperatures ($0° - \sim 100°$K). Now, if the force constants are instead chosen so as to fit the elastic data at 0°K, the frequency of each individual mode of vibration will change significantly, and it may be expected that the corresponding frequency distribution, which would be an approximation to that at low temperatures, will bear no close relation to that calculated in the earlier work. This has here been confirmed by actual calculation and the results given later in this paper show that the results obtained are not in agreement with experiments.

A natural starting point for an investigation of the lattice vibrations would be provided, if the many-electron problem for an ionic solid had been solved with sufficient accuracy. As this is not the case one is forced to proceed in a phenomenological manner and one is then naturally led to consider the information brought out in several investigations of the long polar oscillations of ionic solids,[1] which can be discussed using macroscopic theory. In first place it has been found that the electronic polarization is of essential importance; the main effect being to cut down considerably the limiting frequency of the longitudinal vibrations. It has been anticipated in the literature that the polarisation may effect also other modes of vibrations in a singificant way, although no actual calculations of the effect have been done up to now. Unfortunately, we have not been able in this investigation to include a satisfactory treatment of the polarisation, but have had to limit ourselves to the rather idealized case, where the lattice is considered as an assembly of point-dipoles. We believe that such a treatment cannot be very accurate, but hope that it will at least give the correct trend.

A second effect of importance is concerned with the effective charge. This concept was first introduced by Lyddane Sachs and Teller [10] and was later investigated in more detail by Szigeti [14], who derived by macroscopic considerations a formula expressing the effective charge in wellknown empirical data. He also pointed out that deviations from the ionic charge might be due to a "distortion dipole" caused by the mutual distortion of neighbouring ions. The study of the limiting vibrations gives, however, no idea how the effect should be treated for a general mode of vibration and to proceed it therefore seems necessary to consider a specific model for the interaction between the ions. In a study of the Heitler-London approximation in connexion with lattice vibrations by one of us[2] it was found that the concept of effective charge enters without any ad hoc assumptions and agrees qualitatively with the results of Szigeti. Quantitatively, however, the accuracy of the Heitler-London method is not sufficient to make the method useful for calculations, and therefore the treatment was simplified so that the most important parameters could be determined from empirical data instead of calculated using electronic wave functions. For this investigation, however, we have preferred not to make full use of the formulas in ref. [9], but instead to use a simplified version of that scheme, which will be briefly described in the next section.

Brief dcscription of the theoretical basis of the calculation

The frequencies of each mode of vibration are found from the plane-wave solutions of the equation

$$m_k \frac{d^2}{d\,t^2} \mathbf{u}_k^l = - \sum_{l'k'} \mathbf{\Phi}_{kk'}^{l\,l'} \mathbf{u}_{k'}^{l'}. \tag{1}$$

Here the index l refers to a unit cell, k distinguishes between the particles within a cell, m_k is the mass of the particle at the position k, and $\mathbf{u}_k^l$ denotes the displacement of the particle (l, k) from its equilibrium position. $\mathbf{\Phi}_{kk'}^{l\,l'}$ is a tensor depending on the interaction between the ions and is found from the lattice potential. As the contributions to $\mathbf{\Phi}_{kk'}^{l\,l'}$ due to effective charge modifications and polarisation are discussed in detail in ref. [9], we shall only briefly mention the further simplifications introduced here. The simplification is entirely concerned with the contributions associated with the effective charge. According to the Heitler-London scheme the effective charge is described as a many-body effect, giving rise to terms in $\boldsymbol{\Phi}_{kk'}^{ll'}$ of a rather complicated appearance. In order to simplify the calculations we have neglected most of these terms and only retained the simplest one, having the form of a Coulomb interaction. In this approximation $\boldsymbol{\Phi}_{kk'}^{ll'}$ can be expressed as a sum of three parts

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[1] We refer to [3] for a comprehensive review of this subject.

[2] S. O. Lundqvist [8], [9].

$$\boldsymbol{\Phi}_{kk'}^{ll'} = {}^{\text{coul}}\boldsymbol{\Phi}_{kk'}^{ll'} + {}^{\text{rep}}\boldsymbol{\Phi}_{kk'}^{ll'} + {}^{\text{pol}}\boldsymbol{\Phi}_{kk'}^{ll'}, \tag{2}$$

which will be discussed separately below.

The first part with components

$$ {}^{\text{coul}}\Phi\underset{\alpha\beta}{\overset{ll'}{kk'}} = \eta\, \varepsilon_k\, \varepsilon_{k'}\, e^2 \frac{\partial^2}{\partial\, x\underset{\alpha}{\overset{ll'}{kk'}}\, \partial\, x\underset{\beta}{\overset{ll'}{kk'}}} \left(\frac{1}{|\mathbf{r}_k^l - \mathbf{r}_{k'}^{l'}|} \right) \tag{3}$$

represents the modified Coulomb interaction. Here ε_k and $\varepsilon_{k'}$ denote the valencies of the ions k and k'. e is the elementary charge and the indices α and β refer to the Cartesian components. The parameter η is determined from the average of the elastic constants c_{12} and c_{44} according to the formula[1]

$$\eta = \frac{(c_{12} + c_{44})\, a^4}{0.6954\, e^2} \tag{4}$$

where a is the interionic distance. It should be noted that the deviation from the classic Coulomb interaction in (3) is due to a many-body effect in the interaction potential and does not correspond to a modified two-body Coulomb interaction. We also point out that η is an approximation to $(e^*/e)^2$, e^* being the effective charge appearing in the polarisation term (8) discussed later. In general this approximation is not satisfactory but for KCl η agrees fairly well with the estimate given by Szigeti, and for NaCl the use of (3) anyhow gives an improvement.

The second part

$$ {}^{\text{rep}}\Phi\underset{\alpha\beta}{\overset{ll'}{kk'}} = \frac{\partial^2}{\partial\, x\underset{\alpha}{\overset{ll'}{kk'}}\, \partial\, x\underset{\beta}{\overset{ll'}{kk'}}} \{ V(|\mathbf{r}_k^l - \mathbf{r}_{k'}^{l'}|) \} \tag{5}$$

is mainly due to the repulsive interaction between nearest neighbours.[2] There would of course be no difficulty to include also a central interaction between next nearest neighbours except for the fact that the number of empirical constants is insufficient to determine more parameters. For the calculations we write (5) in the form

$$ {}^{\text{rep}}\Phi\underset{\alpha\beta}{\overset{ll'}{kk'}} = x\underset{\alpha}{\overset{ll'}{kk'}}\, x\underset{\beta}{\overset{ll'}{kk'}}\, Q + \delta_{\alpha\beta} P. \tag{6}$$

Q and P are determined from the equilibrium condition and the elastic constant c_{11} according to

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[1] Because of the approximation introduced here the Cauchy relation $c_{12} = c_{44}$ is automatically fulfilled, so in all calculations we replace either of them by their arithmetic mean.

[2] According to ref. [7] and [8] $V(|\mathbf{r}_k^l - \mathbf{r}_{k'}^{l'}|)$ also contains a part derived from a three-body potential, but which here acts as an ordinary central potential.

$$c_{11} = a\,Q - \frac{\eta\, e^2}{a^4}\cdot 1.569 \tag{7}$$

and

$$P = -\frac{\eta\, e^2}{a^3\cdot 0.2913}. \tag{7'}$$

Before giving the expression for the third part in (2), which describes the effect of the polarization, we introduce two matrices $\mathbf{T}$ and $\boldsymbol{\alpha}$ having the elements

$$T\underset{\alpha\beta}{\overset{ll'}{kk'}} = \frac{\partial^2}{\partial\, x\underset{\alpha}{\overset{ll'}{kk'}}\;\partial\, x\underset{\beta}{\overset{ll'}{kk'}}}\left(\frac{1}{\left|\mathbf{r}_k^l - \mathbf{r}_{k'}^{l'}\right|}\right)$$

and

$$\alpha\underset{\alpha\beta}{\overset{ll'}{kk'}} = \alpha_k\,\delta_{ll'}\,\delta_{kk'}\,\delta_{\alpha\beta}$$

where α_k denotes the polarisability of the ion k.

In this notation

$${}^{\mathrm{pol}}\Phi\underset{\alpha\beta}{\overset{ll'}{kk'}} = \varepsilon_k\,\varepsilon_{k'}\,e^{*2}\left\{\mathbf{T}\,(\boldsymbol{\alpha}^{-1} - \mathbf{T})^{-1}\,\mathbf{T}\right\}\underset{\alpha\beta}{\overset{ll'}{kk'}} \tag{8}$$

where e^* denotes the effective charge. These coefficients are not easy to compute according to (8), but what is needed for the calculations is actually the associated Fourier matrices, and for these the problem reduces to operations on 6×6 matrices only, which can be handled by standard methods.

The calculations have been performed according to the following three approximations:

(a) The Born model in which the polarisation term (8) is neglected and the parameter η in (3) equals one.

(b) An intermediate approximation in which the polarisation is neglected but the parameter η is determined from (4).

(c) Both the polarisation and the modified Coulomb interaction are taken into account according to (3), (4) and (8).

The calculations were done for 89 non-equivalent wave vectors evenly distributed in 1/48 of the reciprocal lattice cell, giving totally 534 frequencies. Tables were prepared for the contributions from the Coulomb and repulsive forces, and the calculation of the polarisation term and the final solution of the secular equations were done using the electronic computer BESK in Stockholm. Approximate frequency distributions $f(\omega)$ have been determined by counting the number of frequencies in intervals of the length $\Delta\omega = 0.2\cdot 10^{-13}$ radians/sec. The distribution functions were normalized such that $\int f(\omega)\,d\omega = 6$. Because of the rather small numbers of frequencies, we have preferred to consider the histograms, instead of drawing continuous curves. Due to the same limitations we have not found it possible to make a closer study of the nature of the singularities in the distribution functions.

The specific heat was calculated from the formula

$$\begin{aligned} C_v &= k\,N\int\frac{x^2\,e^x}{(e^x-1)^2}\,f(\omega)\,d\omega \\ x &= \frac{\hbar\,\omega}{k\,T} \end{aligned} \tag{9}$$

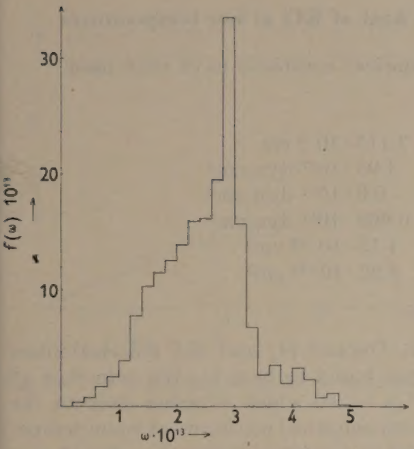

Fig. 1a. The frequency distribution function for KCl according to approximation a.

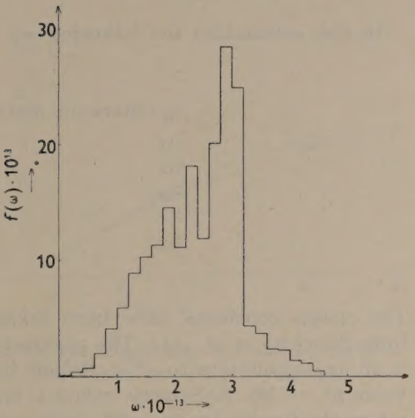

Fig. 1b. The frequency distribution function for KCl according to approximation b.

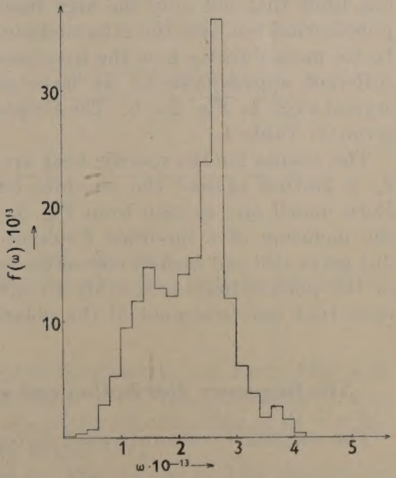

Fig. 1c. The frequency distribution function for KCl according to approximation c.

where N is the number of the oscillators, k Bolzmann's constant, $\hbar = h/2\pi$ where h is Planck's constant, ω are the frequencies of the oscillators, and $f(\omega)$ is the distribution function of lattice vibrations. Part of the uncertainty due to the approximative frequency distribution functions could possibly have been eliminated by expressing C_v as an integral over the reciprocal lattice cell, but due to the tentative nature of our calculation, we preferred to use (9), which leads quicker to results.

The frequency distribution and specific heat of KCl at low temperatures

In this calculation the following set of empirical constants have been used

KCl

a_0 (interionic distance): $3.115 \cdot 10^{-8}$ cm
c_{11}: $4.95 \cdot 10^{11}$ dyn/cm^2
c_{12}: $0.6 \cdot 10^{11}$ dyn/cm^2
c_{44}: $0.669 \cdot 10^{11}$ dyn/cm^2
$\alpha_{\overset{+}{K}}$: $1.13 \cdot 10^{-24}$ cm^3
$\alpha_{\overset{-}{\mathrm{Cl}}}$: $2.92 \cdot 10^{-24}$ cm^3

The elastic constants have been taken from Durand [4] and the polarizabilities from Shockley *et al.* [11]. The parameter η was found to be 0.74. We note that $\eta^{\frac{1}{2}}$ is an approximation to e^*/e. Szigeti finds $e^*/e = 0.80$ which is rather close to the value $\eta^{\frac{1}{2}} = 0.86$. As Szigetis values is found from empirical constants at room temperature the figures are not quite comparable, and we preferred to use the value $e^*/e = 0.86$ in our calculations.

The frequency distributions are given in Figs. 1 a, 1 b and 1 c. A comparison between the curves shows that one important effect of the effective charge and polarisation is to shift the high-frequency part towards lower frequencies. If I b and I c is compared one finds that not only the high frequency part of the spectrum is affected by the polarisation but also the intermediate frequency part ($\sim 2 \cdot 10^{-13}$ rad./sec.). In order to see more directly how the frequencies of the individual modes are changed in the different approximations we have given the curves $\omega = \omega(k)$ for waves along a crystal axes in Fig. 2 a, b. The frequencies according to approximations b and c are given in Table 1.

The results for the specific heat are given in Fig. 3, where the Debye temperature θ_D is plotted against the absolute temperature T. The results obtained from the Born model are, as seen from Fig. 3, far off from the experimental results.[1] Already the inclusion of a modified Coulomb interaction changes the result significantly, but gives still too high values of θ_D over the whole temperature interval. The effect of the polarisations is roughly to shift the whole curve downwards, but it seems clear that our treatment of the polarization overestimates the effect.

The frequency distribution and specific heat of NaCl at low temperatures

The empirical constants used in our calculations for NaCl are

a_0: $2.79 \cdot 10^{-8}$ cm
c_{11}: $5.75 \cdot 10^{11}$ dyn/cm^2
c_{12}: $0.986 \cdot 10^{11}$ dyn/cm^2
c_{44}: $1.327 \cdot 10^{11}$ dyn/cm^2
$\alpha_{\overset{+}{\mathrm{Na}}}$: $0.28 \cdot 10^{-24}$ cm^3
$\alpha_{\overset{-}{\mathrm{Cl}}}$: $2.92 \cdot 10^{-24}$ cm^3

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[1] Note that our treatment differs somewhat from Iona's, which also includes a central interaction between next nearest neighbours.

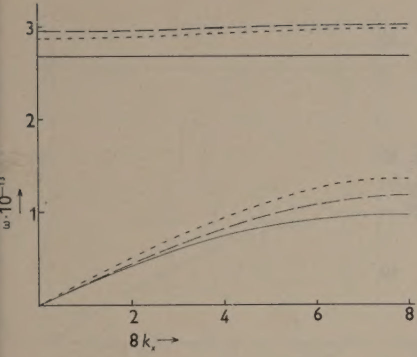


Fig. 2a. The transversal branches of vibration for KCl a) – – – b) — — c) ——.

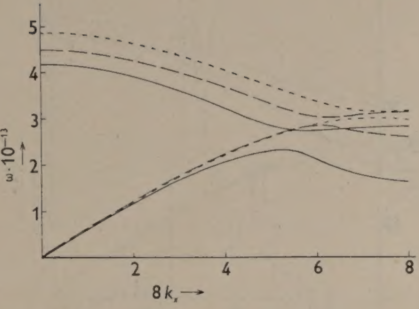
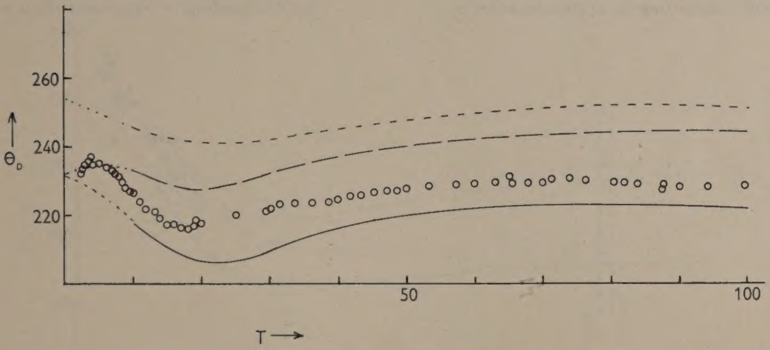


Fig. 2b. The longitudinal branches of vibration for KCl a) – – – b) — — c) ——.



The Debye characteristic temperature for KCl.

Fig. 3. a) – – – b) — — c) ——. The experimental points are taken from Berg and Morrison [2].

The values of the elastic constants are those given by Overton and Swim [10] and the polarisabilities are taken from Shockley et alien [11]. The parameter η was found to be 0.87. This gives a rather poor estimate of the effective charge, $\eta^{\frac{1}{2}} = 0.93$, so for e^*/e we have used the value 0.74 found by Szigeti [12].

The frequency distributions are reproduced in Fig. 4a, b, c. The changes in the distribution function in the different approximations are qualitatively the same but are more accentuated for NaCl. Especially notable is the strong suppression of the high frequency part in (c) compared with (a) as well as the shift of the position and height of the peak occurring approximately at the residual ray frequency. The relation $\omega = \omega(k)$ is given for waves along a crystal axes in Fig. 5, a, b, and shows a significant change due to the polarisation for all modes of vibrations except the acuostical vibrations of long wavelength. The frequencies according to approximations b and c are given in Table 2.

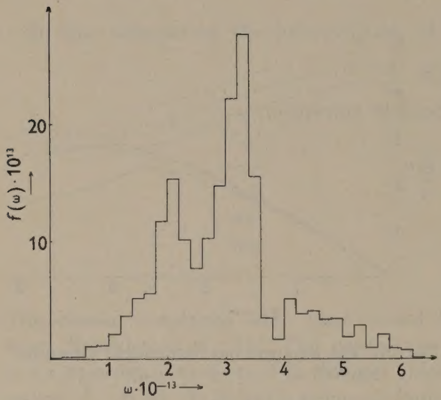


Fig. 4a. The frequency distribution function for NaCl according to approximation a.

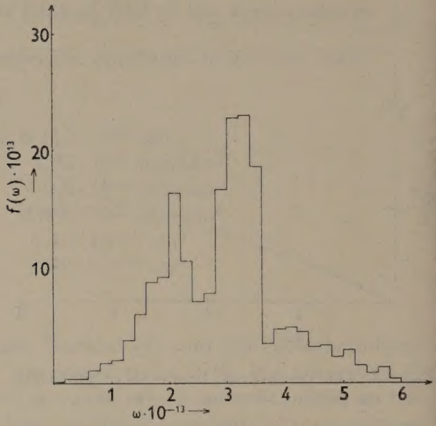


Fig. 4b. The frequency distribution function for NaCl according to approximation b.

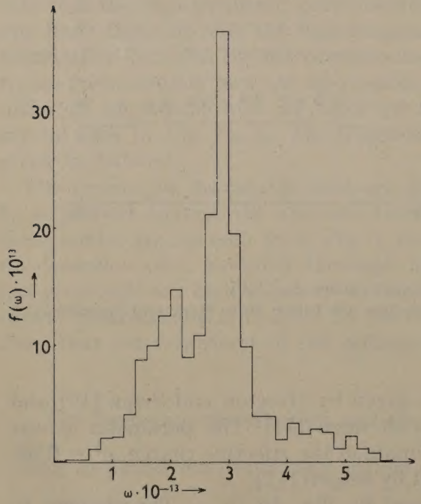


Fig. 4c. The frequency distribution function for NaCl according to approximation c.

The curves of θ_D versus T is shown in Fig. 6. As for KCl the Born approximation is in bad agreement with experiments; the inclusion of a modified Coulomb interaction alone gives some improvement, and together with the polarisation one obtains a strong shift of the whole curve, but the result indicates that the effect of the polarisation is somewhat overestimated in our treatment.

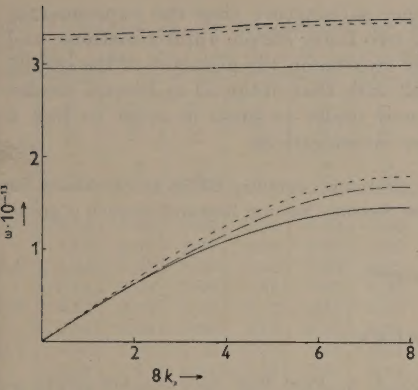


Fig. 5a. The transversal branches of vibration for NaCl a) – – – b) — — c) ——.

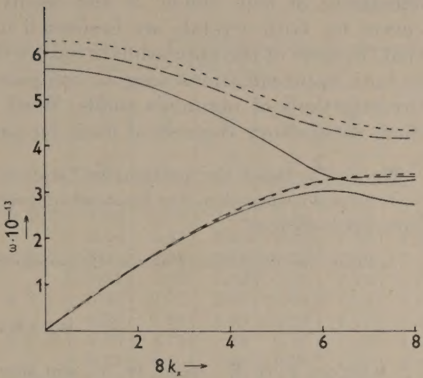
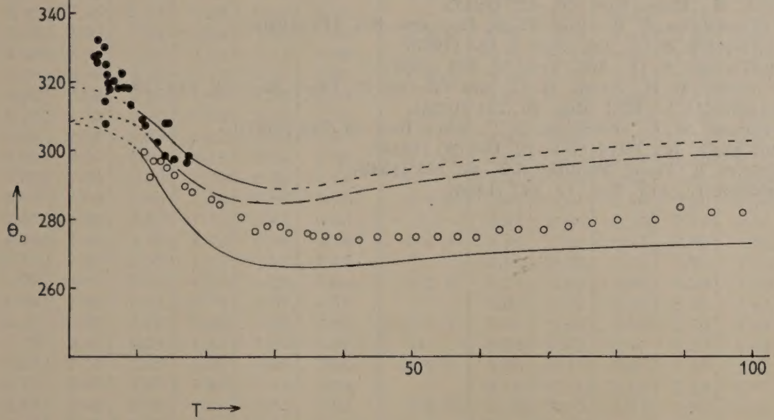


Fig. 5b. The longitudinal branches of vibration for NaCl a) – – – b) — — c) ——.



The Debye characteristic temperature for NaCl.

Fig. 6. a) – – – b) — — c) ——. The experimental points are taken from Clusius, Goldmann, Perlick [4] and Martin [11].

Conclusion

The results show that for both crystals the qualitative features are the same in all three approximations. For both KCl and NaCl the Born model gives results which are not in agreement with experiments. The approximation where only the Coulomb interaction is modified as well as that where the polarisation is included agrees better with experiments; although in none of the cases the agreement is good. This is certainly due to the very approximate theory on which the calculations are based. Nevertheless the results show clearly that both the effective charge modification and the polarisation are of importance and have to be considered in calculations of the vibrations of ionic solids. It also seems rather satisfactory that the experimental curves for both crystals are bracketed in by two fairly simple approximations, and that, in spite of the approximate nature of the treatment, the accuracy of the results in both approximations seem to compare well with that obtained in several similar investigations of non-ionic solids. Work is now under progress in order to find a more satisfactory theoretical basis for further investigations.

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REFERENCES

1. BARRON, T. H. K., BERG, W. T., and MORRISON, J. A., Proc. Roy. Soc. *242*, 478 (1957).
2. BERG, W. T., MORRISON, J. A., Proc. Roy. Soc. *242*, 467 (1957).
3. BORN, M., and HUANG, K., Dynamical Theory of Crystal Lattices, Oxford 1954.
4. CLUSIUS, K., GOLDMAN, I., and PERLICK, A. Z., Naturforsch., *4a*, 424 (1949).
5. DURAND, M. A., Phys. Rev. *50*, 449 (1936).
6. IONA, M., Phys. Rev. *60*, 822 (1941).
7. KELLERMANN, E. W., Phil. Trans. Roy. Soc. *238*, 513 (1940).
8. LUNDQVIST, S. O., Ark. Fys. *9*, 435 (1955).
9. LUNDQVIST, S. O., Ark. Fys. *12*, 263 (1957).
10. LYDDANE, R. H., SACHS, R. G., and TELLER, E., Phys. Rev. *59*, 673 (1941).
11. MARTIN, D. L., Phil. Mag. *46*, 751 (1955).
12. OVERTON, W. C., and SWIM, R. T., Phys. Rev. *84*, 758 (1951).
13. SHOCKLEY, W., Phys. Rev. *70*, 105 (A) (1946).
14. SZIGETI, B. Trans. Faraday Soc. *45*, 155 (1949).
15. TENERZ, E., Ark. Fys. *11*, 247 (1956).

Appendix

able 1. Values of the frequencies for KCl.

For each point the upper value belongs to the approximation b and the lower value to the approximation c. p_α are the components of the wave vector in units of $\frac{1}{8} \cdot (1/2\,a_0)$.

$p_y\,p_z$	$\omega_1 \cdot 10^{-13}$	$\omega_2 \cdot 10^{-13}$	$\omega_3 \cdot 10^{-13}$	$\omega_4 \cdot 10^{-13}$	$\omega_5 \cdot 10^{-13}$	$\omega_6 \cdot 10^{-13}$	$p_x\,p_y\,p_z$	$\omega_1 \cdot 10^{-13}$	$\omega_2 \cdot 10^{-13}$	$\omega_3 \cdot 10^{-13}$	$\omega_4 \cdot 10^{-13}$	$\omega_5 \cdot 10^{-13}$	$\omega_6 \cdot 10^{-13}$
0 0	4.50	2.95	2.95	0.00	0.00	0.00	4 2 2	3.69	2.76	2.54	2.33	1.64	1.33
	4.18	2.68	2.68	0.00	0.00	0.00		3.45	2.55	2.38	2.25	1.56	1.33
0 0	4.44	2.95	2.95	0.61	0.22	0.22	4 3 0	3.57	3.02	2.39	2.30	1.80	1.24
	4.11	2.68	2.68	0.61	0.22	0.22		3.31	2.69	2.30	2.25	1.75	1.06
1 0	4.43	2.95	2.90	0.72	0.58	0.32	4 3 1	3.59	2.91	2.39	2.33	1.83	1.32
	4.11	2.68	2.66	0.72	0.57	0.31		3.35	2.63	2.30	2.29	1.77	1.20
1 1	4.41	2.90	2.90	0.82	0.61	0.61	4 3 2	3.58	2.70	2.46	2.36	1.89	1.52
	4.11	2.65	2.65	0.82	0.61	0.61		3.38	2.50	2.39	2.28	1.82	1.48
0 0	4.28	2.96	2.96	1.21	0.44	0.44	4 3 3	3.48	2.64	2.50	2.32	1.98	1.74
	3.92	2.68	2.68	1.19	0.42	0.42		3.32	2.58	2.36	2.23	1.91	1.74
1 0	4.28	2.96	2.87	1.24	0.73	0.50	4 4 0	3.34	3.03	2.43	2.21	2.09	1.45
	3.96	2.68	2.64	1.22	0.72	0.49		3.11	2.71	2.42	2.17	1.99	1.19
1 1	4.28	2.91	2.85	1.27	0.81	0.71	4 4 1	3.38	2.91	2.49	2.21	2.09	1.52
	3.98	2.65	2.62	1.26	0.80	0.71		3.16	2.62	2.46	2.16	2.00	1.31
2 0	4.20	2.97	2.74	1.39	1.13	0.66	4 4 2	3.38	2.68	2.63	2.20	2.09	1.69
	3.90	2.68	2.57	1.39	1.12	0.63		3.20	2.59	2.45	2.15	2.02	1.59
2 1	4.20	2.89	2.74	1.45	1.15	0.85	4 4 3	3.29	2.85	2.41	2.20	2.09	1.90
	3.92	2.64	2.57	1.44	1.13	0.84		3.15	2.78	2.28	2.13	2.05	1.87
2 2	4.13	2.75	2.75	1.63	1.19	1.19	4 4 4	3.17	3.02	2.20	2.20	2.09	2.09
	3.88	2.56	2.56	1.62	1.19	1.19		3.03	2.96	2.11	2.11	2.07	2.07
0 0	4.01	2.97	2.97	1.75	0.64	0.64	5 0 0	3.31	3.00	3.00	2.60	0.97	0.97
	3.62	2.68	2.68	1.70	0.60	0.60		2.84	2.68	2.68	2.31	0.85	0.85
1 0	4.03	2.98	2.86	1.76	0.86	0.70	5 1 0	3.36	3.01	2.86	2.60	1.13	1.03
	3.67	2.68	2.62	1.72	0.85	0.65		2.97	2.68	2.55	2.31	1.05	0.90
1 1	4.04	2.92	2.83	1.78	0.96	0.84	5 1 1	3.40	2.94	2.80	2.60	1.26	1.10
	3.71	2.65	2.60	1.74	0.93	0.83		3.05	2.65	2.51	2.31	1.15	1.02
2 0	3.99	2.99	2.66	1.83	1.29	0.85	5 2 0	3.37	3.02	2.64	2.56	1.49	1.20
	3.69	2.68	2.51	1.79	1.27	0.78		3.07	2.69	2.46	2.27	1.45	1.02
2 1	4.00	2.90	2.66	1.85	1.33	0.99	5 2 1	3.40	2.92	2.64	2.55	1.58	1.26
	3.72	2.64	2.51	1.82	1.30	0.96		3.13	2.63	2.46	2.27	1.49	1.15
2 2	3.96	2.75	2.62	1.96	1.45	1.26	5 2 2	3.40	2.77	2.66	2.46	1.81	1.41
	3.72	2.56	2.48	1.93	1.41	1.26		3.18	2.54	2.49	2.23	1.67	1.39
3 0	3.83	3.00	2.49	1.98	1.65	1.04	5 3 0	3.26	3.03	2.64	2.30	1.88	1.42
	3.56	2.69	2.41	1.98	1.59	0.92		3.03	2.70	2.48	2.16	1.83	1.16
3 1	3.84	2.91	2.49	2.03	1.66	1.16	5 3 1	3.31	2.91	2.65	2.29	1.94	1.47
	3.59	2.63	2.41	2.02	1.61	1.08		3.09	2.62	2.50	2.16	1.86	1.29
3 2	3.81	2.71	2.50	2.17	1.68	1.42	5 3 2	3.31	2.73	2.69	2.26	2.08	1.60
	3.60	2.52	2.40	2.14	1.64	1.40		3.14	2.58	2.47	2.15	1.93	1.55
3 3	3.69	2.50	2.50	2.40	1.71	1.71	5 3 3	3.23	2.85	2.50	2.27	2.13	1.78
	3.51	2.38	2.38	2.35	1.69	1.69		3.09	2.73	2.34	2.16	1.98	1.78
0 0	3.68	2.99	2.99	2.22	0.82	0.82	5 4 0	3.05	3.05	2.66	2.26	2.04	1.65
	3.23	2.68	2.68	2.09	0.74	0.74		2.86	2.71	2.56	2.15	1.99	1.29
1 0	3.71	2.99	2.87	2.23	1.00	0.88	5 4 1	3.15	2.86	2.70	2.28	2.03	1.70
	3.31	2.68	2.59	2.11	0.96	0.79		2.95	2.60	2.58	2.16	1.98	1.41
1 1	3.73	2.93	2.82	2.24	1.12	0.98	5 4 2	3.16	2.83	2.62	2.33	2.01	1.82
	3.37	2.65	2.55	2.12	1.05	0.94		3.01	2.71	2.41	2.19	1.97	1.67
2 0	3.70	3.00	2.62	2.25	1.39	1.03	5 4 3	3.12	2.98	2.38	2.37	1.98	1.97
	3.38	2.69	2.44	2.16	1.37	0.91		3.00	2.86	2.25	2.21	1.95	1.91
2 1	3.71	2.91	2.61	2.27	1.46	1.13	5 5 0	3.07	2.81	2.68	2.50	1.87	1.84
	3.42	2.63	2.43	2.18	1.41	1.07		2.76	2.73	2.48	2.31	1.84	1.39

Table 1 (*continued*)

$p_x p_y p_z$	$\omega_1 \cdot 10^{-13}$	$\omega_2 \cdot 10^{-13}$	$\omega_3 \cdot 10^{-13}$	$\omega_4 \cdot 10^{-13}$	$\omega_5 \cdot 10^{-13}$	$\omega_6 \cdot 10^{-13}$	$p_x p_y p_z$	$\omega_1 \cdot 10^{-13}$	$\omega_2 \cdot 10^{-13}$	$\omega_3 \cdot 10^{-13}$	$\omega_4 \cdot 10^{-13}$	$\omega_5 \cdot 10^{-13}$	$\omega_6 \cdot 10^{-13}$
5 5 1	3.07	2.83	2.64	2.50	1.91	1.83		2.80	2.69	2.68	1.76	1.15	1.01
	2.86	2.67	2.44	2.31	1.83	1.51	7 1 1	3.08	3.03	2.96	2.57	1.44	1.25
5 5 2	3.05	2.93	2.50	2.48	2.02	1.81		2.82	2.71	2.64	1.74	1.26	1.12
	2.95	2.72	2.32	2.30	1.81	1.76	7 2 0	3.06	3.04	2.90	2.45	1.61	1.40
6 0 0	3.02	3.02	3.00	2.85	1.08	1.08		2.81	2.70	2.66	1.72	1.54	1.13
	2.74	2.68	2.68	2.12	0.92	0.92	7 2 1	3.07	3.02	2.87	2.41	1.75	1.41
6 1 0	3.10	3.02	2.91	2.77	1.23	1.15		2.85	2.71	2.60	1.73	1.59	1.25
	2.82	2.69	2.63	2.09	1.11	0.97	7 2 2	3.06	2.97	2.80	2.28	2.04	1.51
6 1 1	3.15	2.96	2.90	2.70	1.37	1.19		2.87	2.69	2.56	1.89	1.63	1.46
	2.88	2.64	2.63	2.07	1.22	1.08	7 3 0	3.06	3.05	2.73	2.22	1.98	1.65
6 2 0	3.09	3.03	2.88	2.53	1.56	1.32		2.78	2.71	2.58	1.98	1.63	1.27
	2.88	2.69	2.60	2.02	1.50	1.09	7 3 1	3.05	3.02	2.70	2.19	2.10	1.65
6 2 1	3.15	2.92	2.88	2.50	1.68	1.35		2.83	2.70	2.53	2.03	1.61	1.39
	2.94	2.64	2.59	2.01	1.56	1.21	7 3 2	3.05	2.94	2.63	2.37	2.08	1.70
6 2 2	3.14	2.90	2.78	2.38	1.95	1.46		2.86	2.69	2.43	2.20	1.63	1.56
	2.99	2.62	2.53	2.01	1.73	1.43	7 4 0	3.08	3.03	2.48	2.33	1.94	1.91
6 3 0	3.05	2.98	2.86	2.25	1.94	1.56		2.75	2.73	2.39	2.30	1.53	1.40
	2.84	2.71	2.57	1.99	1.84	1.23	7 4 1	3.04	3.02	2.48	2.39	1.92	1.91
6 3 1	3.09	2.91	2.83	2.24	2.03	1.58		2.81	2.70	2.36	2.34	1.54	1.49
	2.91	2.64	2.56	2.02	1.84	1.35	7 5 0	3.09	3.02	2.64	2.16	2.13	1.67
6 3 2	3.09	2.91	2.67	2.27	2.15	1.66		2.76	2.76	2.52	2.04	1.49	1.40
	2.97	2.65	2.45	2.14	1.82	1.59	8 0 0	3.13	3.03	3.03	2.59	1.18	1.18
6 3 3	3.05	2.93	2.50	2.48	2.02	1.81		2.81	2.68	2.68	1.62	0.97	0.97
	2.95	2.72	2.32	2.30	1.81	1.76	8 1 0	3.13	3.03	2.99	2.55	1.31	1.25
6 4 0	3.07	2.91	2.71	2.31	1.96	1.81		2.80	2.69	2.69	1.61	1.16	1.02
	2.77	2.73	2.49	2.24	1.77	1.36	8 1 1	3.12	3.01	2.97	2.50	1.47	1.27
6 4 1	3.05	2.91	2.65	2.37	1.95	1.83		2.80	2.75	2.64	1.59	1.28	1.13
	2.85	2.67	2.46	2.26	1.77	1.47	8 2 0	3.12	3.04	2.86	2.41	1.63	1.43
6 4 2	3.03	2.94	2.52	2.50	1.91	1.90		2.79	2.70	2.68	1.57	1.57	1.14
	2.92	2.68	2.38	2.29	1.77	1.69	8 2 1	3.11	3.01	2.85	2.37	1.78	1.43
6 5 0	3.08	2.91	2.61	2.40	2.05	1.71		2.78	2.77	2.60	1.64	1.56	1.26
	2.79	2.75	2.42	2.22	1.63	1.46	8 2 2	3.10	2.94	2.79	2.24	2.07	1.52
6 5 1	3.05	2.94	2.63	2.37	2.08	1.70		2.81	2.77	2.52	1.88	1.52	1.47
	2.86	2.69	2.43	2.20	1.63	1.56	8 3 0	3.10	3.06	2.65	2.20	2.00	1.68
6 6 0	3.10	2.94	2.79	2.24	2.07	1.52		2.76	2.72	2.58	1.99	1.51	1.28
	2.81	2.77	2.52	1.88	1.52	1.47	8 3 1	3.09	3.02	2.64	2.16	2.13	1.67
7 0 0	3.08	3.02	3.02	2.69	1.15	1.15		2.76	2.76	2.52	2.04	1.49	1.40
	2.79	2.68	2.68	1.77	0.96	0.96	8 4 0	3.08	3.08	2.41	2.30	1.95	1.95
7 1 0	3.08	3.03	3.00	2.62	1.29	1.22		2.74	2.74	2.40	2.29	1.41	1.41

Table 2. Values of the frequencies for NaCl.

For each point the upper value belongs to the approximation b and the lower value to the approximation c. p_α are the components of the wave vector in units of $\frac{1}{8} \cdot (1/2\,a_0)$.

$p_y\, p_z$	$\omega^1 \cdot 10^{-13}$	$\omega_2 \cdot 10^{-13}$	$\omega_3 \cdot 10^{-13}$	$\omega_4 \cdot 10^{-13}$	$\omega_5 \cdot 10^{-13}$	$\omega_6 \cdot 10^{-13}$	$p_x\, p_y\, p_z$	$\omega_1 \cdot 10^{-13}$	$\omega_2 \cdot 10^{-13}$	$\omega_3 \cdot 10^{-13}$	$\omega_4 \cdot 10^{-13}$	$\omega_5 \cdot 10^{-13}$	$\omega_6 \cdot 10^{-13}$
0 0	6.02	3.32	3.32	0.00	0.00	0.00	4 2 2	4.99	3.17	3.01	2.80	1.97	1.60
	5.67	2.95	2.95	0.00	0.00	0.00		4.69	2.91	2.86	2.63	1.88	1.60
0 0	5.95	3.33	3.33	0.71	0.32	0.32	4 3 0	4.86	3.48	2.85	2.69	2.00	1.77
	5.59	2.95	2.95	0.71	0.32	0.32		4.54	2.99	2.80	2.65	1.88	1.58
1 0	5.92	3.34	3.27	0.89	0.63	0.46	4 3 1	4.87	3.37	2.86	2.77	2.04	1.76
	5.58	2.95	2.94	0.89	0.63	0.45		4.58	2.98	2.81	2.67	1.91	1.66
1 1	5.89	3.27	3.27	1.06	0.71	0.71	4 3 2	4.85	3.13	3.04	2.82	2.11	1.82
	5.57	2.94	2.94	1.06	0.70	0.70		4.63	3.02	2.81	2.72	1.98	1.79
0 0	5.76	3.35	3.35	1.39	0.63	0.63	4 3 3	4.74	3.32	2.91	2.80	2.15	1.96
	5.36	2.95	2.95	1.37	0.62	0.62		4.61	3.22	2.77	2.73	2.03	1.92
1 0	5.75	3.35	3.25	1.45	0.88	0.73	4 4 0	4.58	3.53	2.88	2.73	2.18	2.07
	5.39	2.95	2.93	1.44	0.87	0.71		4.30	3.02	2.88	2.71	2.03	1.80
1 1	5.74	3.29	3.23	1.54	0.99	0.88	4 4 1	4.60	3.41	3.00	2.73	2.18	2.05
	5.41	2.94	2.93	1.52	0.98	0.88		4.34	3.06	2.84	2.71	2.03	1.88
2 0	5.64	3.37	3.11	1.71	1.25	0.95	4 4 2	4.61	3.27	3.15	2.72	2.19	2.05
	5.32	2.96	2.90	1.71	1.20	0.91		4.42	3.21	2.78	2.71	2.04	2.00
2 1	5.63	3.29	3.11	1.82	1.28	1.08	4 4 3	4.57	3.53	2.86	2.72	2.19	2.12
	5.34	2.93	2.90	1.80	1.24	1.07		4.49	3.40	2.73	2.71	2.05	2.05
2 2	5.54	3.13	3.13	2.10	1.36	1.36	4 4 4	4.53	3.65	2.72	2.72	2.19	2.19
	5.29	2.89	2.89	2.08	1.34	1.34		4.51	3.49	2.71	2.71	2.05	2.05
0 0	5.46	3.37	3.37	2.00	0.92	0.92	5 0 0	4.70	3.44	3.44	2.94	1.39	1.39
	4.99	2.96	2.96	1.96	0.88	0.88		3.94	2.97	2.97	2.80	1.26	1.26
1 0	5.46	3.38	3.26	2.04	1.11	1.00	5 1 0	4.69	3.45	3.35	2.94	1.52	1.48
	5.03	2.96	2.93	1.99	1.09	0.96		4.00	2.97	2.96	2.77	1.44	1.33
1 1	5.45	3.31	3.23	2.08	1.24	1.09	5 1 1	4.69	3.38	3.33	2.94	1.71	1.48
	5.07	2.94	2.93	2.03	1.21	1.07		4.05	2.98	2.94	2.75	1.60	1.40
2 0	5.39	3.40	3.05	2.16	1.48	1.22	5 2 0	4.64	3.48	3.15	2.91	1.83	1.71
	5.05	2.97	2.88	2.13	1.43	1.14		4.09	2.99	2.93	2.71	1.79	1.52
2 1	5.38	3.31	3.05	2.24	1.54	1.29	5 2 1	4.64	3.38	3.15	2.93	2.01	1.65
	5.07	2.94	2.87	2.19	1.48	1.26		4.13	2.99	2.91	2.70	1.91	1.58
2 2	5.32	3.14	3.02	2.46	1.67	1.47	5 2 2	4.61	3.19	3.16	2.97	2.24	1.72
	5.07	2.88	2.86	2.40	1.61	1.47		4.21	3.04	2.85	2.68	2.14	1.71
3 0	5.18	3.44	2.89	2.40	1.80	1.49	5 3 0	4.48	3.52	3.07	2.77	2.14	2.02
	4.89	2.98	2.82	2.40	1.68	1.37		4.08	3.01	2.96	2.66	2.05	1.75
3 1	5.18	3.34	2.89	2.50	1.81	1.54	5 3 1	4.50	3.41	3.10	2.81	2.25	1.94
	4.91	2.95	2.81	2.47	1.70	1.47		4.13	3.06	2.89	2.66	2.12	1.81
3 2	5.14	3.11	2.89	2.76	1.85	1.68	5 3 2	4.51	3.25	3.16	2.87	2.34	1.92
	4.93	2.88	2.80	2.68	1.76	1.66		4.21	3.18	2.80	2.66	2.23	1.89
3 3	4.99	3.06	2.90	2.90	1.90	1.90	5 3 3	4.46	3.46	2.92	2.90	2.33	2.02
	4.85	2.99	2.79	2.79	1.83	1.83		4.27	3.35	2.74	2.68	2.23	1.99
0 0	5.09	3.41	3.41	2.53	1.17	1.17	5 4 0	4.23	3.58	3.07	2.77	2.34	2.23
	4.50	2.96	2.96	2.45	1.09	1.09		3.92	3.04	3.03	2.65	2.13	1.98
1 0	5.09	3.42	3.30	2.54	1.33	1.26	5 4 1	4.28	3.45	3.17	2.81	2.31	2.20
	4.55	2.97	2.94	2.44	1.28	1.17		3.98	3.17	2.89	2.66	2.16	2.04
1 1	5.09	3.35	3.27	2.57	1.49	1.30	5 4 2	4.35	3.39	3.17	2.83	2.27	2.16
	4.60	2.95	2.94	2.45	1.43	1.26		4.10	3.32	2.76	2.67	2.22	2.07
2 0	5.03	3.44	3.06	2.60	1.67	1.48	5 4 3	4.42	3.56	2.91	2.81	2.24	2.16
	4.61	2.98	2.88	2.49	1.62	1.35		4.29	3.44	2.71	2.69	2.18	2.06
2 1	5.03	3.34	3.06	2.65	1.78	1.49	5 5 0	3.93	3.65	3.08	2.94	2.62	2.11
	4.65	2.95	2.88	2.52	1.71	1.44		3.65	3.07	3.06	2.69	2.18	2.09

Table 2 (*continued*)

$p_x p_y p_z$	$\omega_1 \cdot 10^{-13}$	$\omega_2 \cdot 10^{-13}$	$\omega_3 \cdot 10^{-13}$	$\omega_4 \cdot 10^{-13}$	$\omega_5 \cdot 10^{-13}$	$\omega_6 \cdot 10^{-13}$	$p_x p_y p_z$	$\omega^1 \cdot 10^{-13}$	$\omega_2 \cdot 10^{-13}$	$\omega_3 \cdot 10^{-13}$	$\omega_4 \cdot 10^{-13}$	$\omega_5 \cdot 10^{-13}$	$\omega_6 \cdot 10^{-13}$
5 5 1	4.05	3.48	3.20	2.93	2.54	2.10		3.23	3.04	2.99	2.81	1.62	1.
	3.72	3.23	2.87	2.69	2.25	2.08	7 1 1	4.11	3.51	3.42	3.23	1.99	1.
5 5 2	4.23	3.41	3.17	2.93	2.43	2.07		3.26	3.09	2.94	2.78	1.81	1.
	3.93	3.34	2.71	2.70	2.34	2.05	7 2 0	4.03	3.53	3.40	3.13	2.04	2.
6 0 0	4.37	3.47	3.47	3.20	1.55	1.55		3.26	3.09	3.01	2.68	2.00	1.
	3.40	3.02	2.98	2.98	1.37	1.37	7 2 1	4.01	3.53	3.35	3.12	2.31	1.
6 1 0	4.35	3.48	3.41	3.17	1.67	1.65		3.32	3.11	2.93	2.65	2.17	1.
	3.47	3.03	2.98	2.90	1.55	1.45	7 2 2	3.96	3.50	3.26	3.06	2.62	1.
6 1 1	4.34	3.43	3.40	3.15	1.88	1.62		3.38	3.13	2.88	2.59	2.48	1.
	3.53	3.03	2.94	2.88	1.73	1.51	7 3 0	3.87	3.59	3.30	2.93	2.34	2.
6 2 0	4.27	3.51	3.32	3.04	1.95	1.89		3.26	3.12	3.04	2.50	2.32	1.
	3.58	3.04	3.00	2.75	1.91	1.64	7 3 1	3.89	3.56	3.25	2.95	2.59	2.
6 2 1	4.27	3.44	3.31	3.04	2.19	1.78		3.35	3.13	2.96	2.48	2.45	1.
	3.64	3.06	2.93	2.74	2.06	1.68	7 3 2	3.93	3.50	3.10	3.09	2.68	2.
6 2 2	4.24	3.36	3.21	3.05	2.46	1.81		3.49	3.18	2.86	2.67	2.39	2.
	3.73	3.12	2.83	2.67	2.35	1.79	7 4 0	3.72	3.67	3.18	2.81	2.68	2.
6 3 0	4.11	3.56	3.26	2.84	2.25	2.22		3.24	3.08	3.08	2.54	2.25	2.
	3.60	3.07	3.03	2.60	2.12	1.89	7 4 1	3.82	3.58	3.15	2.97	2.57	2.
6 3 1	4.14	3.47	3.26	2.88	2.44	2.05		3.33	3.16	2.99	2.55	2.28	2.
	3.66	3.13	2.94	2.59	2.31	1.91	7 5 0	3.79	3.62	3.20	2.96	2.67	2.
6 3 2	4.18	3.35	3.18	3.01	2.51	2.00		3.24	3.13	2.96	2.50	2.41	2.
	3.79	3.23	2.80	2.60	2.44	1.97	8 0 0	4.14	3.50	3.50	3.31	1.69	1.
6 3 3	4.23	3.41	3.17	2.93	2.43	2.07		3.24	2.98	2.98	2.72	1.46	1.
	3.93	3.34	2.71	2.70	2.34	2.05	8 1 0	4.09	3.51	3.47	3.29	1.80	1.
6 4 0	3.90	3.63	3.20	2.82	2.55	2.28		3.23	3.02	2.92	2.69	1.65	1.
	3.52	3.09	3.06	2.60	2.22	2.12	8 1 1	4.04	3.53	3.43	3.25	2.02	1.
6 4 1	3.99	3.50	3.20	2.96	2.46	2.25		3.22	3.11	2.94	2.66	1.84	1.
	3.59	3.20	2.93	2.61	2.27	2.13	8 2 0	3.96	3.54	3.38	3.19	2.07	2.
6 4 2	4.14	3.36	3.22	3.01	2.37	2.19		3.19	3.10	3.01	2.59	2.03	1.
	3.79	3.31	2.80	2.64	2.32	2.10	8 2 1	3.93	3.56	3.34	3.15	2.36	1.
6 5 0	3.73	3.70	3.12	2.94	2.83	2.06		3.20	3.18	2.92	2.57	2.21	1.
	3.40	3.11	2.96	2.70	2.32	2.04	8 2 2	3.84	3.60	3.23	3.04	2.70	1.
6 5 1	3.93	3.50	3.10	3.09	2.68	2.05		3.31	3.15	2.82	2.59	2.47	1.
	3.49	3.18	2.86	2.67	2.39	2.02	8 3 0	3.81	3.60	3.23	3.00	2.37	2.
6 6 0	3.84	3.60	3.23	3.04	2.70	1.90		3.14	3.14	3.05	2.44	2.37	1.
	3.31	3.15	2.82	2.59	2.47	1.86	8 3 1	3.79	3.62	3.20	2.96	2.67	2.
7 0 0	4.19	3.49	3.49	3.30	1.65	1.65		3.24	3.13	2.96	2.50	2.41	2.
	3.22	2.98	2.98	2.88	1.44	1.44	8 4 0	3.69	3.69	3.14	2.72	2.72	2.
7 1 0	4.14	3 50	3.46	3.26	1.77	1.75		3.09	3.09	3.14	2.51	2.23	2.

Tryckt den 4 april 1959

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